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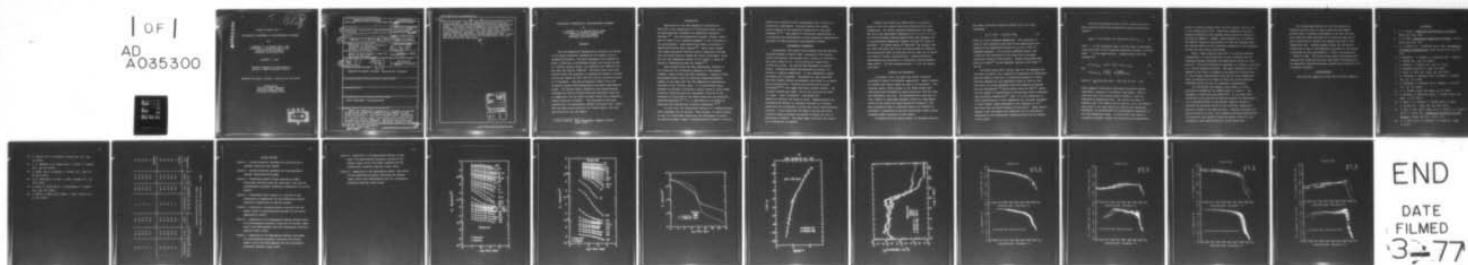
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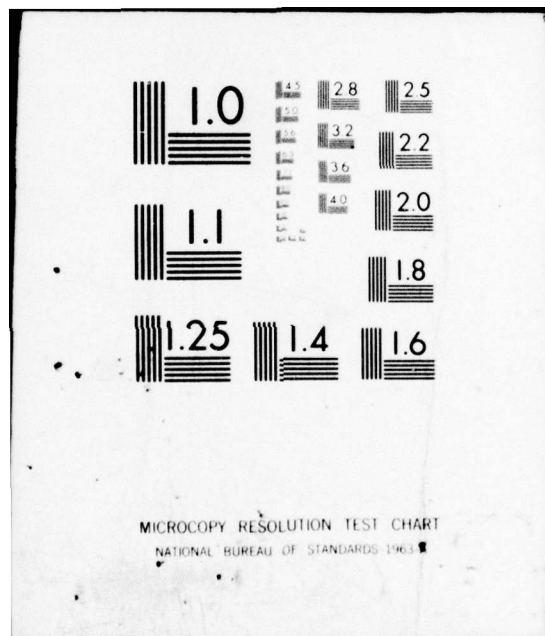
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Technical Report No. 9

VISCOELASTIC PROPERTIES OF POLY(ETHYLENE-G-STYRENE)

by

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ABSTRACT

The Time Temperature Superposition Principle was applied to the stress relaxation isotherms of two samples of poly-(ethylene-g-styrene). The graft copolymers were prepared by mutual irradiation of polyethylene powder and styrene monomer in a nuclear reactor source, one containing 12% (PEGS/12) and the other 58% styrene (PEGS/58). The shift factor data when plotted versus the reciprocal of temperature yielded a straight line in the region of -20°C and 70°C with an activation energy of 32 kcal/mole. From the viscoelastic master curves the relaxation spectra were determined by the second approximation method. The dynamic moduli computed by the interconversion technique can then be shifted from the logarithmic time axis to temperature axis by using the shift factor data obtained in stress relaxation isotherms. The calculated curves were compared with the experimental dynamic mechanical data. Agreement was semi-quantitative for the storage moduli, but only qualitative for the loss moduli.

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INTRODUCTION

Application of the Time Temperature Superposition Principle to the construction of viscoelastic master curves has been eminently successful for homogeneous amorphous polymers.¹⁻³ For semi-crystalline polymers, however, there does not seem to be a complete agreement in the literature on its applicability. Some workers have found it necessary to employ the vertical shift factors;⁴⁻⁷ while others showed that simple horizontal shifting would be sufficient provided that the strain does not exceed the linear viscoelastic range and that the temperature remains in the region in which the degree of crystallinity does not change.⁸⁻¹¹

More recently there has been considerable interest in the studies of the viscoelastic behavior of heterogeneous polymers, such as block and graft copolymers. Because of their heterophase nature, they are generally thermorheologically complex in the sense that the Time Temperature Superposition Principle is not strictly valid. It is nevertheless still possible to construct viscoelastic master curves by using simple horizontal shifting along the logarithmic time axis if the procedure is restricted to the region where only one relaxation mechanism dominates,^{12,13} or if some method is available for separating the contributing relaxation mechanisms.^{14,15}

In this work, the viscoelastic behavior of a semicrystalline graft copolymer will be studied. This material is rather complex in that it is both semi-crystalline and heterophase in nature. The specific polymer chosen is poly(ethylene-g-styrene), primarily

because the respective parent homopolymers have already been extensively investigated. Previous workers have studied various aspects of the mechanical properties of this graft copolymer.¹⁶⁻¹⁸ The purpose of the present communication is to scrutinize the applicability of Time Temperature Superposition Principle to semi-crystalline multicomponent polymers.

EXPERIMENTAL TECHNIQUES

Polyethylene (PE) pellets were obtained from the Phillips Petroleum Company as Marlex 6009. According to the manufacturer's information, this polymer has a density of 0.960 gm/c.c., and a melt index of 0.9. Its M_w and M_n are respectively 133,000 and 12,000. The pellets were dissolved in boiling xylene. Polyethylene powder was obtained by cooling a 1% solution to ambient temperature. It was subsequently washed by benzene and by methanol. The powder was then mixed with distilled styrene monomer and methanol, and sealed in an ampule after nitrogen purge. Grafting was carried out by mutual irradiation¹⁹⁻²⁰ with gamma rays from a nuclear reactor. Two radiation dosages were used: one at 0.25 mrad and the other at 1 mrad. After irradiation, the polymer was washed with methanol and dried in vacuo. Homopolystyrene was extracted with benzene in a Soxhlet extractor for 24 hours. Composition was determined by weight gain and by carbon-hydrogen analysis. It was found that the sample receiving the lower radiation dosage contained 12% styrene by weight and will be designated as PEGS/12. The other sample contained 58% styrene and is designated as PEGS/58.

Samples were molded into sheet forms in a hydraulic press at 150°C for several hours and cooled slowly to room temperature. For stress relaxation experiments, the sample was cut to the approximate dimensions of 0.15 x 0.5 x 5.0 cm³. An Instron Universal Testing Machine Model TMS equipped with a Conrad-Missimer Temperature Chamber was used for these experiments. For moduli above 10⁹ dynes/cm², the flexural mode was used; and below that value the tensile mode was employed. The strains were kept to less than 0.5% in order not to exceed the limits of linear viscoelasticity. Dynamic mechanical measurements were performed on a Rheovibron Viscoelastometer Model DDV-II. For this purpose thinner (~ 0.02 cm) samples were used.

RESULTS AND DISCUSSION

In Figures 1 and 2 are shown the stress relaxation isotherms of PEGS/12 and PEGS/58 respectively. Moduli obtained by flexural and tensile modes are seen to be consistent. Viscoelastic master curves (Figure 3) for these samples were constructed from isotherms by simple horizontal shifting along the logarithmic time axis. The extraordinarily wide span of time (around 30 logarithmic decades) covered by these master curves is not unusual for semi-crystalline polymers.⁶ The more precipitous drop in relaxation modulus for PEGS/58 is obviously a consequence of the high polystyrene content, which undergoes glass transition in this region.

In constructing the master curves for amorphous polymers,

the rubber elasticity correction factor (T/T_0) was often introduced:

$$E_r(T, a_T t) = E_r(T_0, t) T/T_0 \quad (1)$$

where T_0 is the reference temperature. The correction is valid in such instances since most of the superposition was applied to the temperature region of T_g to $T_g + 100^\circ\text{C}$ of amorphous polymers. For our graft copolymer system, the utility of this correction is not clear due to the semi-crystalline nature of the material. Similar conclusions were drawn by Faucher¹⁰ and by Nakayasu, Markowitz and Plazek¹¹ for PE.

The shift factor data ($\log a_T$) used for the superposition are given in Figure 4 as a function of reciprocals of temperature. From the slope of this plot, an activation energy of 32 kcal/mole was obtained for the temperature range of -40°C to 70°C . This value is in good agreement with those reported by Faucher for pure polyethylene¹⁰ and by Locke & Paul for PEGS.¹⁸ Above 70°C the degree of crystallinity of PE has been found to decrease with increasing temperature.¹⁰ Thus, it is not surprising to find a discontinuity at this temperature for the graft copolymer. In their dynamic creep measurement of PE, Nakayasu, et al.¹¹ have found the activation energy of 28 kcal/mole. These workers, however, used a procedure that separated out two contributing mechanisms to the viscoelastic relaxation which was not adopted in this paper.

From the viscoelastic master curves, relaxation spectra were calculated using the Ferry-Williams second approximation method:²

$$H_{2B}(\tau) = -2.303 M(m) E(t) d \log E(t) / d \log t |_{t = \tau} \quad (2)$$

where τ is the relaxation time, m is the slope of the doubly logarithmic plot of the relaxation spectrum, and $M(m) = 1/\Gamma(1+m)$ where Γ is the gamma function. Dynamic moduli were then computed by²

$$E'(\omega) |_{\omega=1/\tau} = E(t) + H(\tau) \psi(m) |_{\tau=1/\omega} \quad (3)$$

and

$$E''(\omega) |_{\omega=1/\tau} = \left(\frac{H\pi}{2} \right) \sec\left(\frac{m\pi}{2}\right) |_{\tau=1/\omega} \quad (4)$$

where $H = H_{2B}/2.303$ and $\psi(m) = (\pi/2) \csc(m\pi/2) - \Gamma(m)$.

These computed viscoelastic functions are plotted against logarithmic frequency or reciprocal time scales. Then by using the shift factor data given in Figure 4, they are converted to temperature axis. The results are given in Figures 6 and 7 for PEGS/12 and in Figures 8 and 9 for PEGS/58. Also given in the same figures are similar data separately determined on the Rheovibron at corresponding frequencies in the same temperature range. It can be seen that there is reasonable agreement between the calculated and experimental

values of dynamic storage moduli for both samples, particularly in the regions below 110°C. Above this temperature the short plateaus predicted by the computed curves cannot be verified in the data for PEGS/12. However, these plateaus are in evidence for PEGS/58 (Figure 8) particularly for the low frequency data. The expected shifts in the transition temperatures with frequency changes are also clearly discernable.

Table 1 shows numerical data for E' at several selected temperatures. It can be seen that in most instances the discrepancies between calculated and experimental values are less than 20%. Such semi-quantitative agreement is, however, restricted to a limited temperature region. The upper temperature limit is imposed by the onset of changes in the degree of crystallinity, in this instance approximately 70°C; and the lower temperature limit is defined by the region in which the stress-relaxation isotherms become too flat for meaningful superposition.

For the dynamic loss moduli, there seems to be only qualitative resemblance for PEGS/12 shown in Figure 7. The agreement is especially poor below 20°C. On the other hand, similarity in the qualitative features between the experimental and calculated results is improved for PEGS /58 (Figure 9), although the predicted shifts in the transition temperatures are not as great as the observed ones. This poor agreement may partly be due to the fact that transient mechanical measurements are generally less sensitive than the dynamic mechanical measurements at low temperatures or at high frequencies.

The limited applicability of the Time Temperature Superposition Principle to semi-crystalline heterophase polymers here is perhaps attributable to the fact that any errors may have been cancelled out in using the same set of shift factor data to convert the computed data back to the temperature axis. Another possible reason for the partial success may be due to the temperature proximity of the primary relaxations for both polyethylene ($\sim 120^{\circ}\text{C}$) and polystyrene ($\sim 100^{\circ}\text{C}$) in PEGS. Thus with caution simple time-temperature superposition technique may yield some useful information for the apparently thermorheologically complex semi-crystalline multicomponent polymers.

ACKNOWLEDGMENT

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Table 1. Calculated and Experimental Dynamic Storage
Moduli for Poly(ethylene-g-styrene)

Temperature (°C)	E' (10^{10} dynes/cm ²) at 110 Hz			E' (10^{10} dynes/cm ²) at 11 Hz		
	Expt'l	Cal'd	% Discrepancy	Expt'l	Cal'd	% Discrepancy
PEGS/12						
0	3.10	3.20	3	2.95	3.20	8
20	2.65	3.09	17	2.55	3.09	21
40	2.20	2.51	14	1.97	2.40	22
60	1.70	1.93	14	1.44	1.81	26
80	1.20	1.38	15	0.99	1.32	33
PEGS/58						
0	3.30	3.33	1	3.10	3.27	5
20	2.97	3.20	8	2.81	3.06	9
40	2.62	2.87	10	2.42	2.68	11
60	2.33	2.38	2	1.93	2.23	16
80	1.82	1.85	2	1.48	1.75	18

FIGURE CAPTIONS

Figure 1: Stress-relaxation isotherms for poly(ethylene-g-styrene) containing 12% styrene.

Figure 2: Stress-relaxation isotherms for poly(ethylene-g-styrene) containing 58% styrene.

Figure 3: Viscoelastic master curves obtained by simple horizontal shifting along the logarithmic time axis for poly(ethylene-g-styrene) containing respectively 12 and 58% styrene.

Figure 4: Logarithmic shift factors as a function of the reciprocals of temperature for poly(ethylene-g-styrene) containing respectively 12 and 58% styrene.

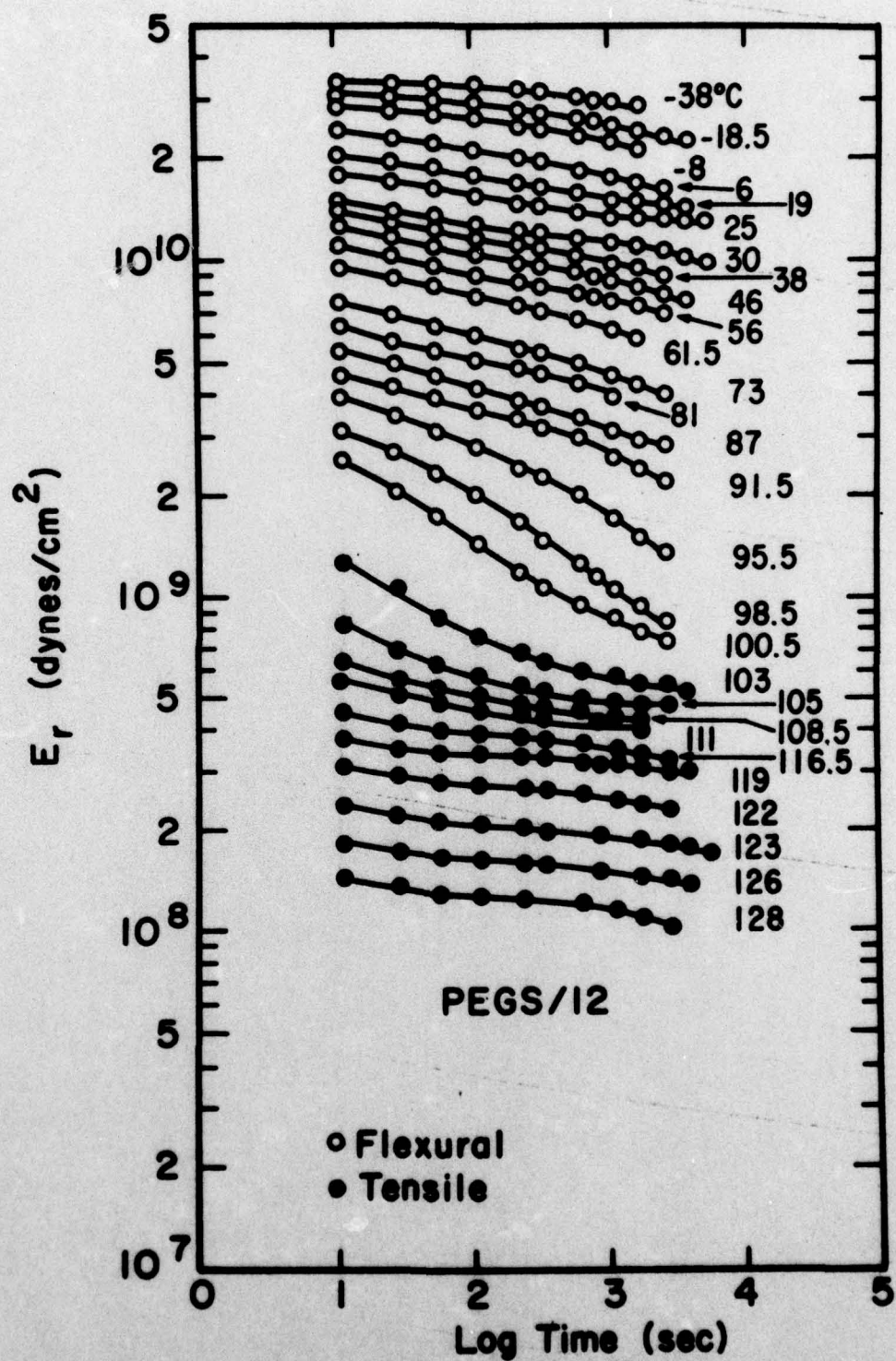
Figure 5: Viscoelastic relaxation spectra obtained from the master curves of poly(ethylene-g-styrene) by the second approximation method.

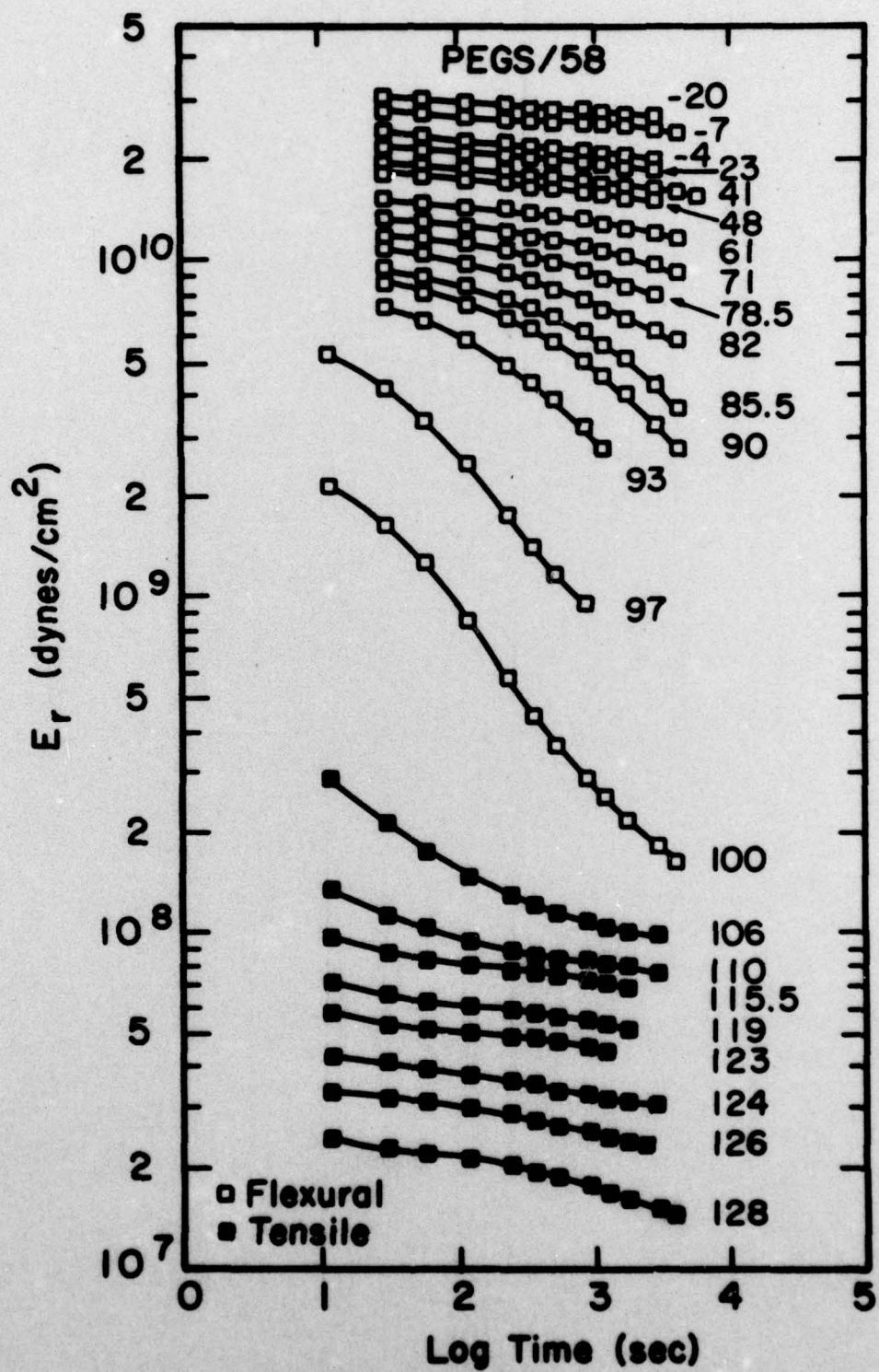
Figure 6: Comparison of the experimental dynamic storage moduli for poly(ethylene-g-styrene) containing 12% styrene (upper curve) with those computed from the viscoelastic relaxation spectrum (lower curve).

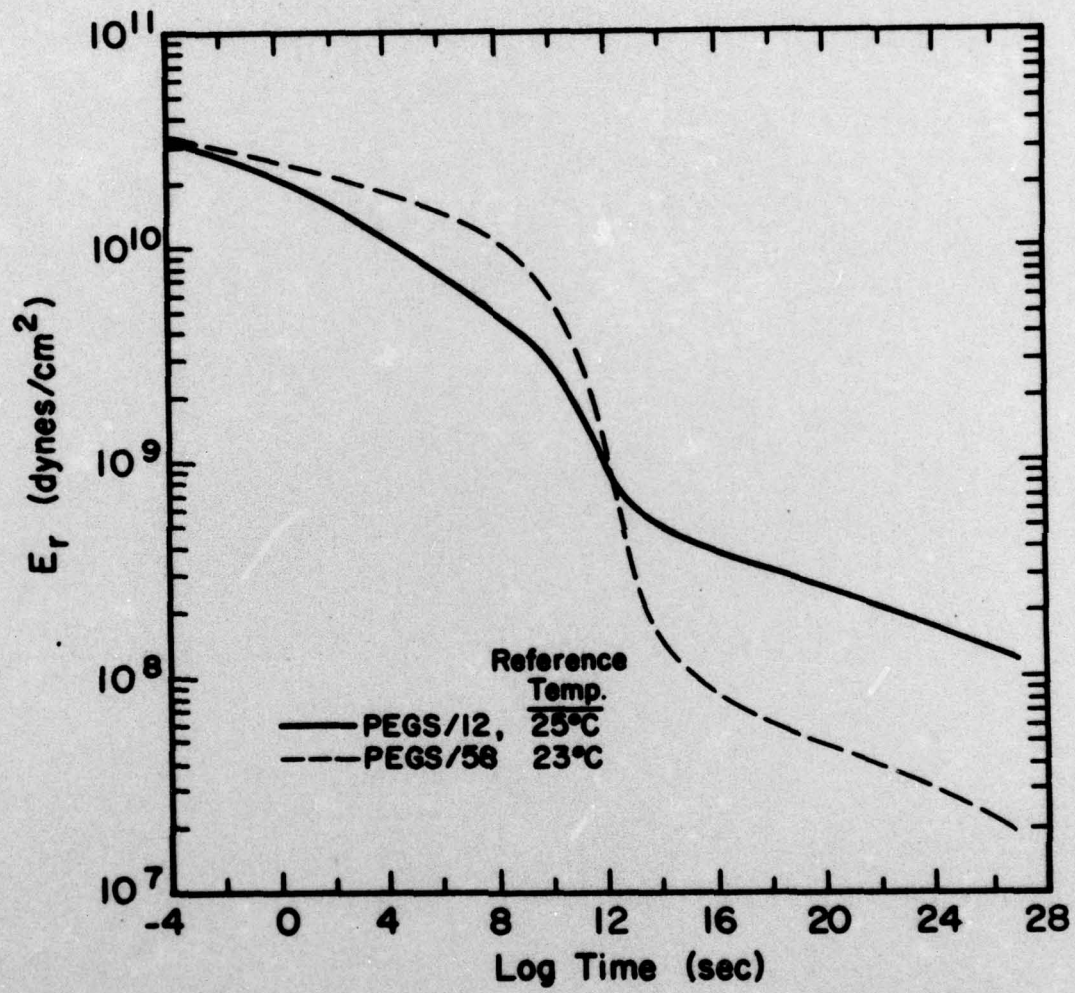
Figure 7: Comparison of the experimental dynamic loss moduli for poly(ethylene-g-styrene) containing 12% styrene (upper curve) with those computed from the viscoelastic relaxation spectrum (lower curve).

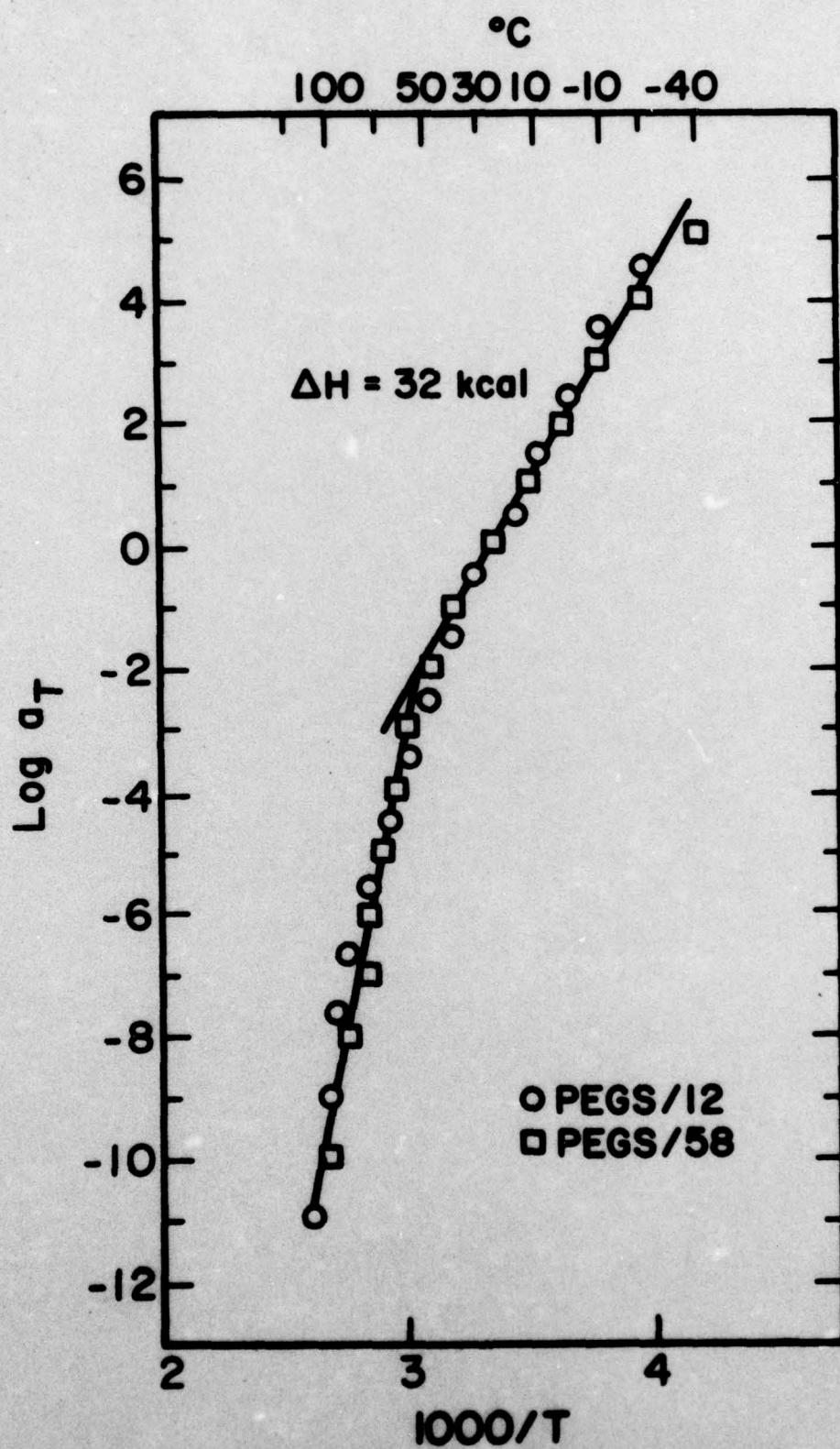
Figure 8: Comparison of the experimental dynamic storage moduli for poly(ethylene-g-styrene) containing 58% styrene (upper curve) with those computed from the viscoelastic relaxation spectrum (lower curve).

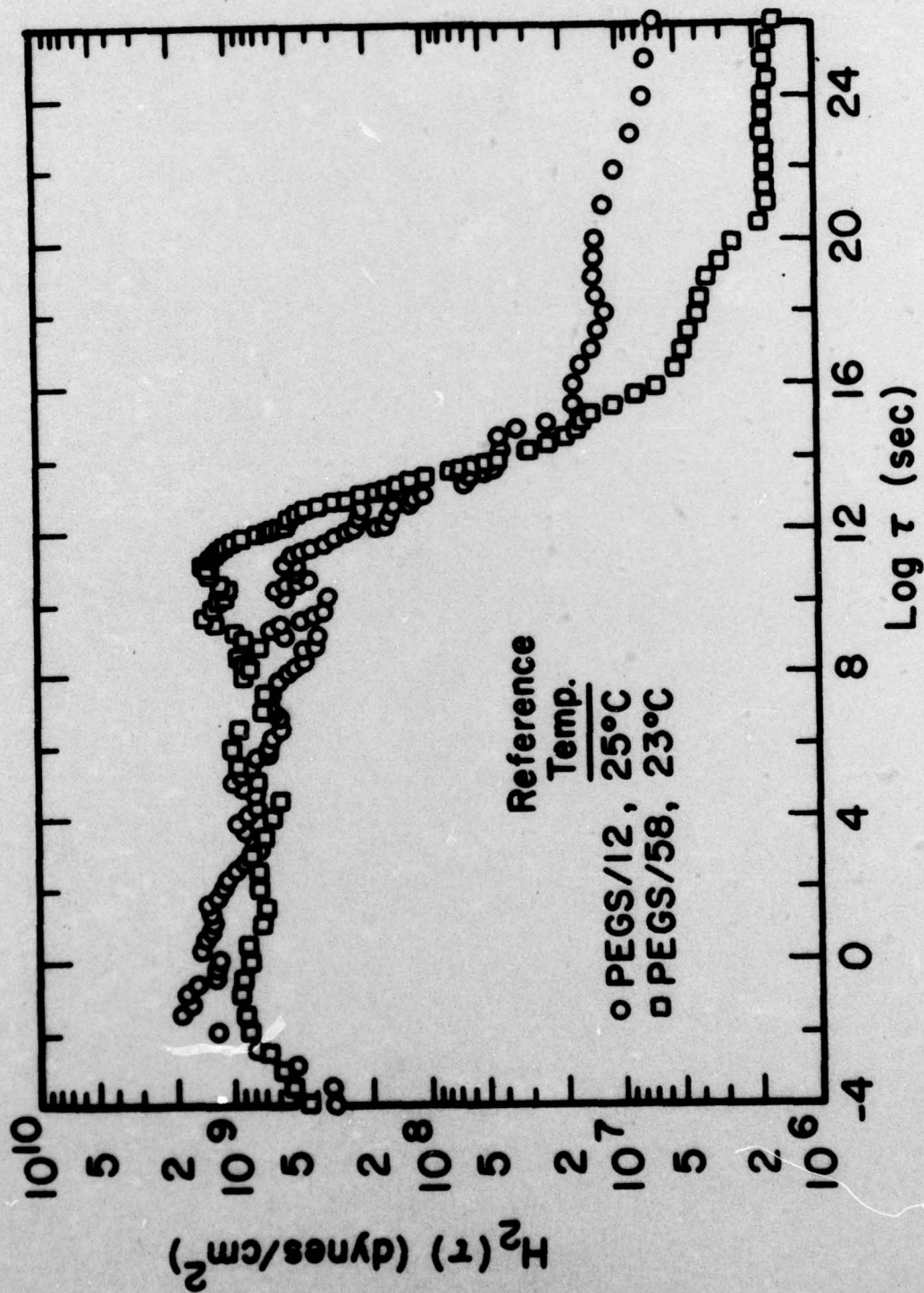
Figure 9: Comparison of the experimental dynamic loss moduli for poly(ethylene-g-styrene) containing 58% styrene (upper curve) with those computed from the viscoelastic relaxation spectrum (lower curve).



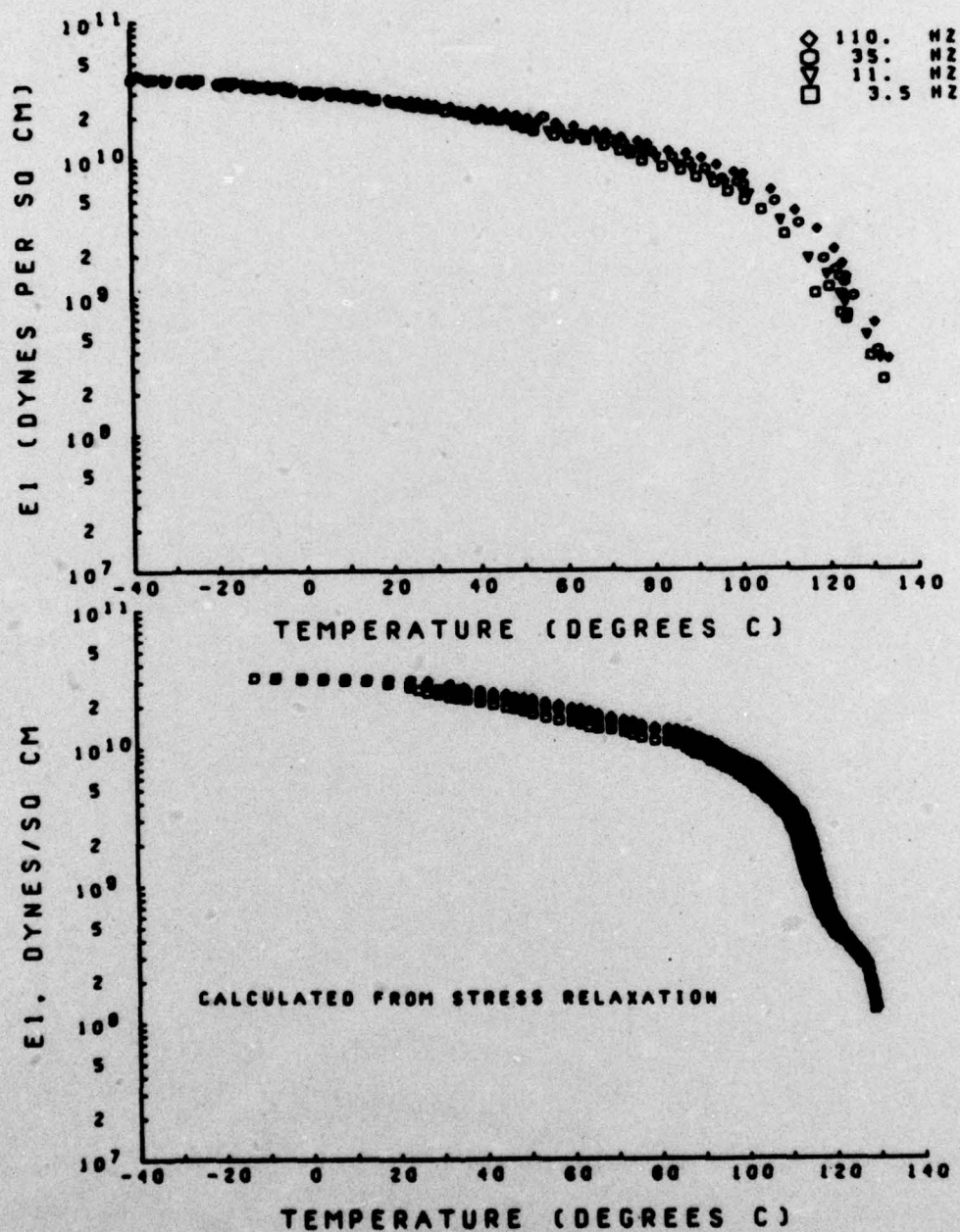




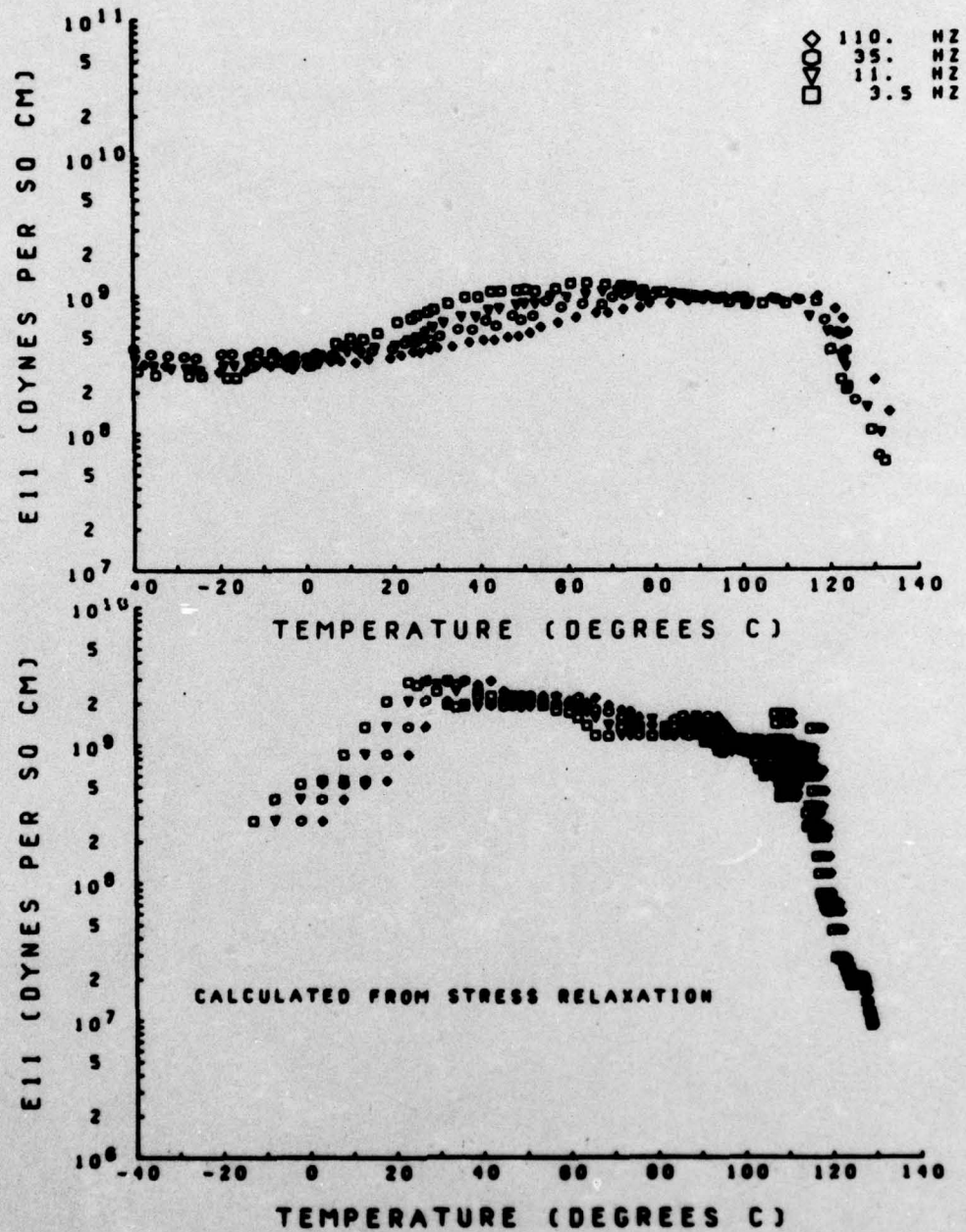




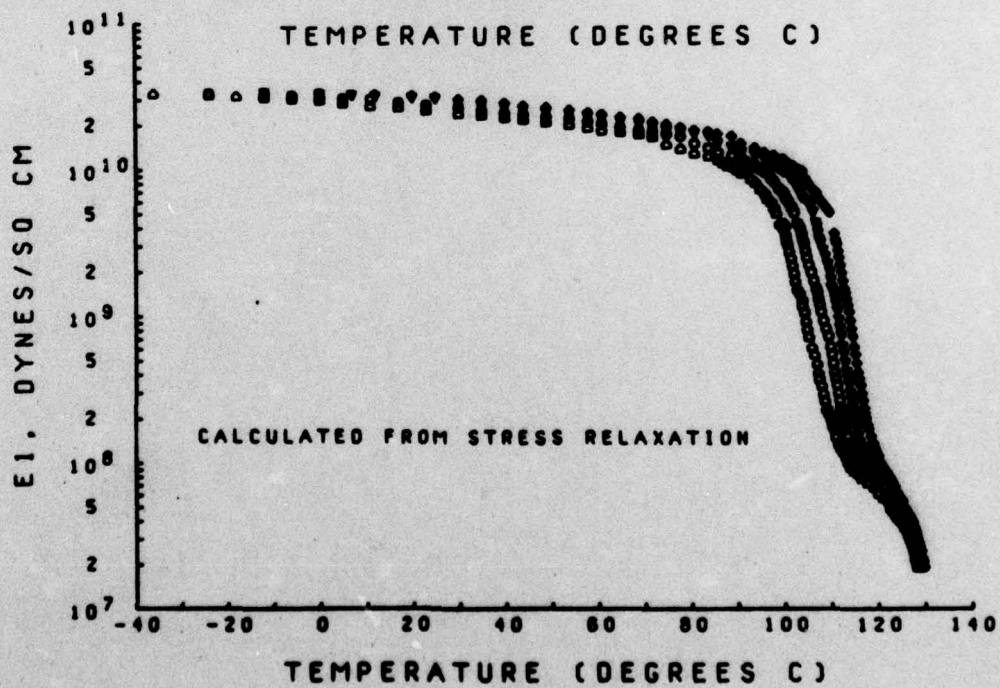
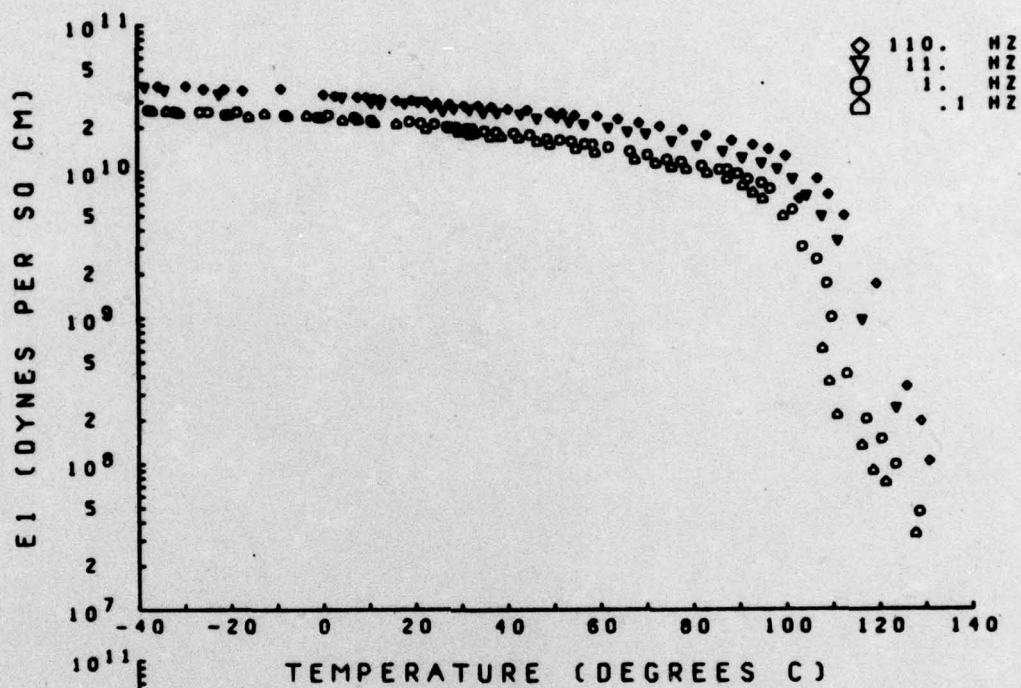
PEGS/12



PEGS/12



PEGS/58



PEGS/58

